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Ambient Ozone Measurements In the National Parks Using Passive Samplers
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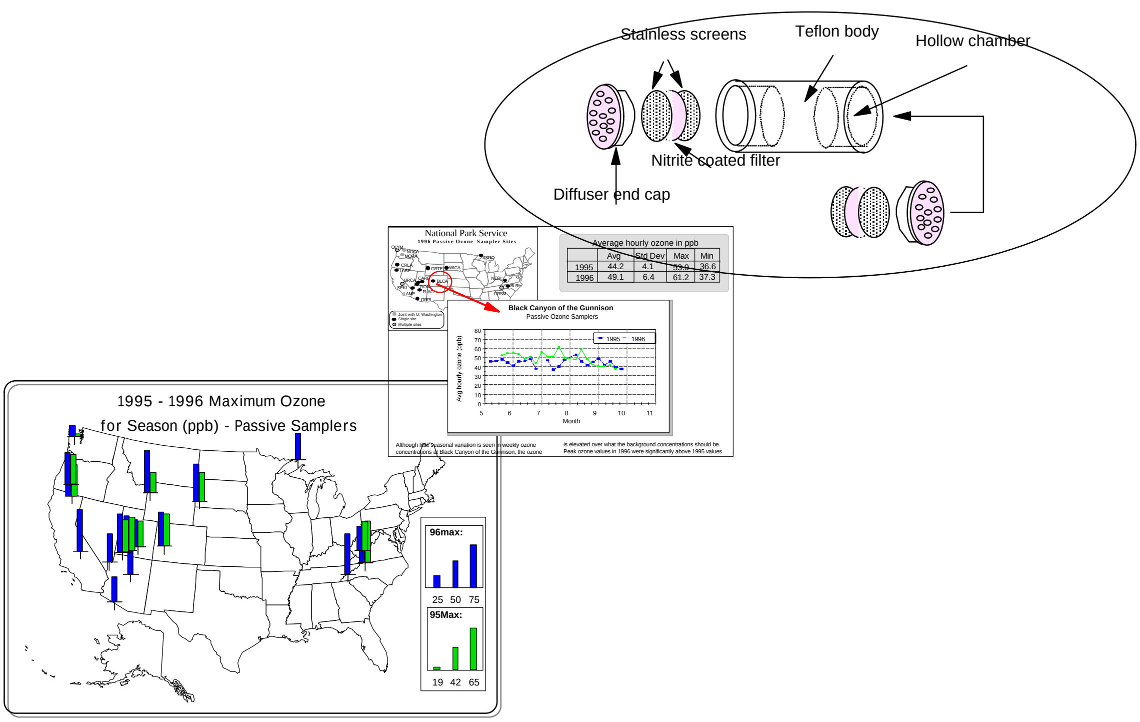

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Ambient Ozone Measurements in the National Parks Using Passive Samplers 1995 – 1996

Quick Summary

Ambient ozone concentrations were measured to provide baseline data in National Park Service (NPS) areas designated as Clean Air Act Class I for which no ozone data was previously available. These weekly ozone measurements, using passive samplers, have been made in 22 park units for periods ranging from 3 weeks to 4 months during the summers of 1995 and 1996. No areas with exceptional high ozone concentrations were found in parks that participated in this program. However, ozone concentrations were often above the expected background levels and approached concentrations that may be of concern for biological effects. Significant variation was see between nearest parks. The spatial distribution studies conducted as part of this program showed that ozone concentrations vary considerably even within a park or between parks that are fairly close. The passive ozone sampling program is presented as an alternative to the much more expensive regulatory guideline monitoring. The method has been shown to provide useful information on air pollutant levels in the parks and should be continued.

Introduction and Background

Air pollution is an external threat to the resources of many national parks. Ozone pollution has been shown to adversely affect human health and to injure sensitive plants species. Since the early 1980s, the Air Resources Division of the NPS has operated a nation-wide network of continuous ozone analyzers to monitor ozone levels and trends in the NPS units. A plan was formulated in 1991 to have a series of baseline and trends sites that eventually would provide monitoring data at each of the 48 Class I areas administered by NPS and several Class II areas. Because funding has not been adequate to complete that plan, continuous monitoring has been delayed at a number of park units. In order to address this delay, the passive ozone monitoring program was initiated to provide a low-cost means to obtain ozone concentration data for those areas that have not yet been monitored.

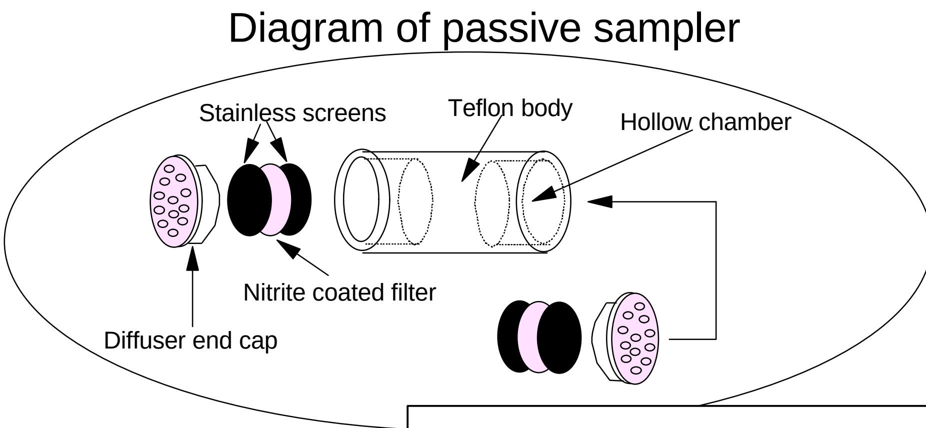
The Air Resources Division has tested (Ray et. al, 1993, 1994) passive ozone samplers that are low cost, simple to use, and do not require power to operate. The devices are similar to filter samplers in that they provide integrated measurements and the actual analysis is done later at a laboratory. The passive samplers can provide information on ozone concentrations and thus provide a baseline by which the need for additional, more intensive, monitoring can be judged. There are several uses for data collected using passive samplers. Measurements over several years can be used to determine trends in ozone pollution at a specific park and estimate the maximum expected annual ozone concentrations. Also, estimates can be made of how representative the next closest continuous ozone monitors can characterize ozone levels within that park. The results from the passive ozone samplers reduce the uncertainty of the geographical extent of ozone pollution in the parks and provide the first real observations for many of the park units involved in the program.

How can the results from the passive samplers be used and interpreted? Because the measurement is an integrated ozone exposure, typically over a one-week period, the results can not be compared directly to the National Ambient Air Quality Standard (NAAQS) for ozone that is based on one-hour ozone averages. The devices are also not designated as equivalent methods for measuring ozone by EPA. However, the measurements can indicate if ozone exposures are high enough to present a risk to plant and animal resources, can provide baseline ozone information for trend comparisons, and can be used for research purposes. Some researchers believe that extended high-ozone exposures can be as harmful as short-duration ozone exposures that exceed the 0.12 ppm (parts per million) NAAQS ozone standard. EPA has proposed changes to the current primary and secondary standards to cover extended ozone exposures and, hence, more relevant to protection of park resources. EPA is considering cumulative exposure indices for daytime ozone concentrations exceeding 60 ppb and summing to greater than 25,000 ppb-hrs over three-months, and for eight-hour averages that exceed 80 ppb.

This report contains the observed ozone concentrations for parks that participated in the passive sampling program. It provides a basic level of comparison of ozone concentrations between different parks and identifies areas where ozone concentrations are high. Both seasonal and between-year differences are examined. In those parks where multiple locations were sampled, spatial variations in ozone are discussed. This report is a first stage in the analysis and will be followed by additional reports on prediction of maximum hourly ozone concentration for a season, spatial differences in ozone in complex terrain, and representativeness of the nearest continuous ozone monitors to parks that did passive ozone sampling.

Air Monitoring with Passive Samplers

Ogawa passive samplers were selected after extensive testing for use in NPS units. Ogawa samplers consist of a double-sided filter holder that is mounted on a “badge” with a clip on the back. Inside the filter holder are two nitrite-coated filters. Air flow into the sampler depends solely on diffusion, i.e., there is no active components in the sampler to draw air in. When the nitrite-coated filters are exposed to ambient air, ozone diffuses through the endcaps and reacts with the nitrite to form nitrate. A rainshield of PVC plastic protects the samplers from direct contact with water and sunlight in field use (see Figure 1) to avoid artifacts or low readings.



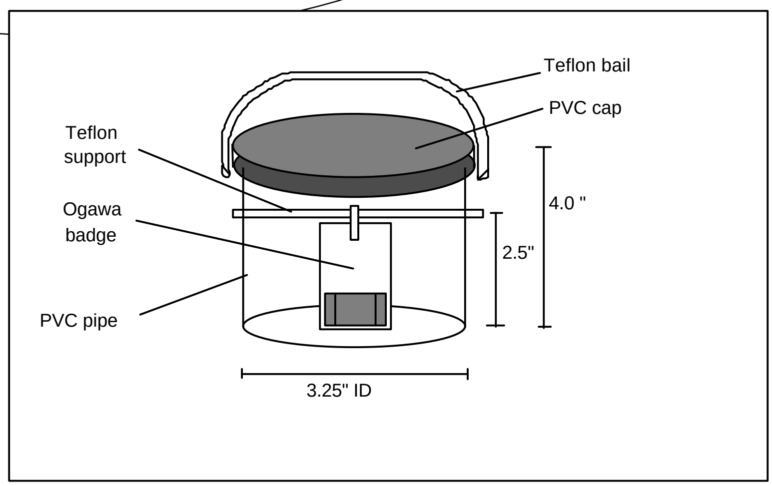


Figure 1. Diagrams of the passive sampler device and of the rainshield with the sampler "badge" inside. The rainshield is made from 3-inch diameter pvc drain pipe, a pvc end-cap, and Teflon tubing for supports

Proceedure

The passive samplers are shipped to the field sites inside amber plastic vials and zip-closure plastic bags. When field personnel remove the sampler from the protective containers exposure time begins. After a measured time of exposure (normally one week), the samplers are returned to the shipping containers and sent to a lab for analysis. At the lab, the filters are removed in an ozone-free atmosphere, the filter extracted with water, and the extract analyzed by ion chromatography for nitrate ion. The mass of the nitrate is used to calculate the ozone dose or the average ozone hourly concentration determined by dividing ozone dose by the exposure time.

Passive samplers are shipped to the park once a month. Each shipment contains enough samplers for each exposure period during the month plus "blanks" that are not exposed, and some samplers for duplicate exposures. Each plastic vial containing a passive sampler has a label for the date and times to be recorded. In addition, the dates, times, sample numbers, and local observations are recorded on a log sheet At the end of the month, park personnel return the exposed samplers and associated blanks in the shipping box to the lab using a prepaid shipping label.

The on-site equipment consists of a pvc plastic-pipe "tower" and a pair of pvc rainshields that remain at the sampling site. The passive samplers come mounted on badges that clip to the support inside the rainshields.

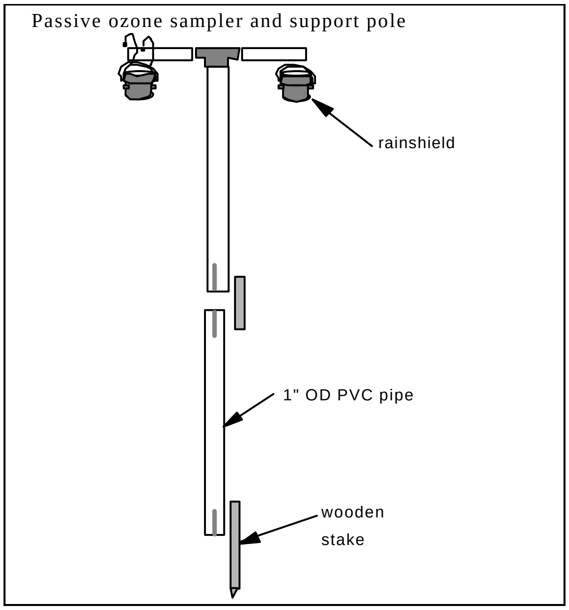


Figure 2. Diagram of the pvc support structure to hold the passive samplers for field sampling of ozone concentrations. The inexpensive support structure disassembles for easy shipment and for sample changes.

Sampling Locations

Parks participating in the passive sampling program fell into three general types: 1) Class I areas that were to get ozone monitoring based on the 1991 NPS Monitoring Strategy, 2) parks that asked to participate, or 3) parks that wanted to conduct ozone spatial distribution studies. The participating parks are shown in Table I for 1994-1997. In general, the sampling locations were in remote areas away from human activity or any other ozone monitoring (see Table A1 for site information). Except for the spatial distribution studies, the ozone measurements were the first that had been done in most of the selected parks.

Most selected parks had just one sampling location and sampled for 3 to 5 months in the summer. A few parks had multiple sampling locations to aid in the determination of the spatial variability of ozone concentration. In some cases, passive samplers were located near vegetation plots that were being studied for ozone injury. In addition, a number of samplers were collocated with continuous ozone-monitoring stations (Table II) to check on the accuracy and precision of the passive ozone measurements.

Table I. List of park units that have participated in passive ozone sampling.

National Park Unit	State	Code	1994	1995	1996	1997	Comments
Black Canyon of the Gunnison	Colorado	BLCA		1	1	1	
Blue Ridge Parkway	North Carolina	BLRI		3	1	2	
Bryce Canyon	Utah	BRCA		1	1	1	
Capital Reef	Utah	CARE		1	1	1	
Crater Lake	Oregon	CRLA		1	1	1	
Denali	Alaska	DENA		1			
Grand Teton	Wyoming	GRTE		1	1	1	
Great Smoky Mountains	Tennessee	GRSM	M	M	M		
Isle Royale	Michigan	ISRO			1	1	
Joshua Tree	California	JOTR					
Lake Mead	Arizona	LAME			3	3	
Lava Beds	California	LABE		1	1	1	
Mount Rainier	Washington	MORA		18	18	18	w/ U. of WA
New River Gorge	West Virginia	NERI		1	1	1	
Noatak	Alaska	NOAT		1			
North Cascades	Washington	NOCA			6		w/ U. of WA
Olympic	Washington	OLYM		6	6	8	w/ U. of WA
Organ Pipe Cactus	Arizona	ORPI			1	1	
Rocky Mountain	Colorado	ROMO	9			3	
Sequoia-Kings Canyon	California	SEKI	M		6	2	
Sunset Crater Volcano	Arizona	SUCR			1	1	
Walnut Canyon	Arizona	WACA			1	1	
Wind Cave	South Dakota	WICA		1	1	1	
Wrangell-St. Elias	Alaska	WRST		1			
Wupatki	Arizona	WUPA			1	1	
Yosemite	California	YOSE				2	
Zion	Utah	ZION		1	1	1	

Numbers are the sites sampled in that park unit
M = multiple sites as part of a research projects

Table II. Parks with collocated continuous analyzers and passive ozone samplers

Park	Site name	Code	1994	1995	1996	1997
Olympic, AQ station	Site 1	OLYM		X	X	X
Great Smoky Mt., Cove Mt.	Cove Mt.	GRSM	X		X	
Denali	AQ station	DENA		X		
Sequoia, Lower Kaweah	Site 6	SEKI	X		X	X
Mt. Rainier	Tohoma Woods	MORA	X	X	X	
North Cascades	AQ station	NOCA			X	
Rocky Mt., AQ station	Site A	ROMO	X			
Channel Islands	AQ station	CHIS				X
Number of sites =			4	3	5	3

Estimates of Sampler Performance

The performance of the passive samplers is monitored by using duplicate samplers to estimate measurement precision and by comparing measurements with continuous ozone analyzers to estimate accuracy. All data is reviewed according to the quality assurance plan to reject samples that had handling problems or were known to be exposed incorrectly. Outlier values are examined carefully to look for problems. However, they are not rejected unless a problem can be identified. Both years had similar precision and accuracy. For comparison to the current values in Table III, in the 1991 passive ozone study (Ray et. al, 1993), the pooled standard deviation was 2.82 ppb. The performance of the passive samplers is as expected or slightly better. The precision is 2% relative standard deviation (RSD) and the accuracy within ±10 %.

Table III. Passive Sampler Performance Indicators

	-------- Precision ---------			------ Accuracy ------	
Year	N	Pooled Std Dev	Percent RSD	N	Mean Absolute % Difference
1995	218	1.36	2.42	5	<10
1996	202	2.05	2.04	39	7.7

RSD – relative standard deviation, in percent
Precision – replicability of repeated measurements
Accuracy – agreement of passive samplers with fully calibrated continuous ozone analyzers

Liu et. al (1995) found the correlation of passive samplers to continuous analyzer data in a Toronto, Canada study was 0.87 with the slope of the regression line of 0.96±0.02. The relative error for 7-day samples was 5% or 0.4 ppb.
Tables A3 and A4 in the appendix summarize the ozone concentrations for 1995-1996 for all the passive ozone sampling locations. Blank cells in the tables indicate either that samples were not taken during that time or that the samples were invalidated. Refer to the site identification Table A1 for information to compare sites within a park.

Results of the ozone passive sampling program

Comparison of seasonal average ozone between parks

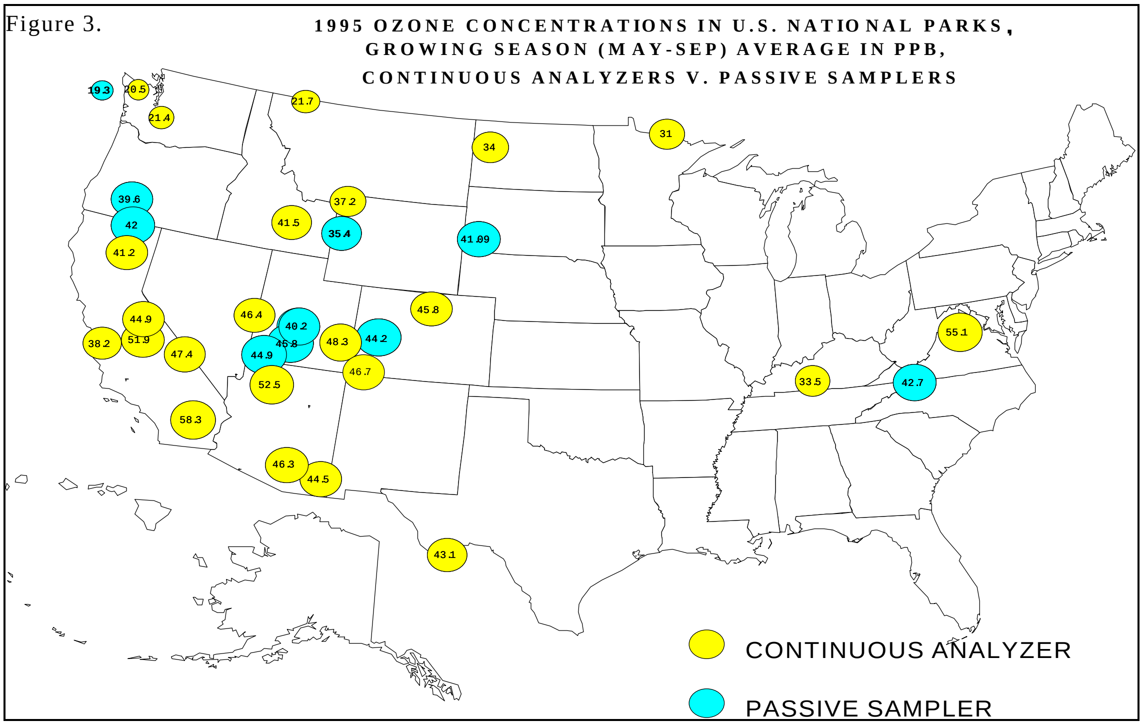


Figure 3. Map of the passive sampling locations in 1995. Open-circle locations tested SO_2 and NOx passive samplers. Stared locations had colocated continuous ozone monitors.

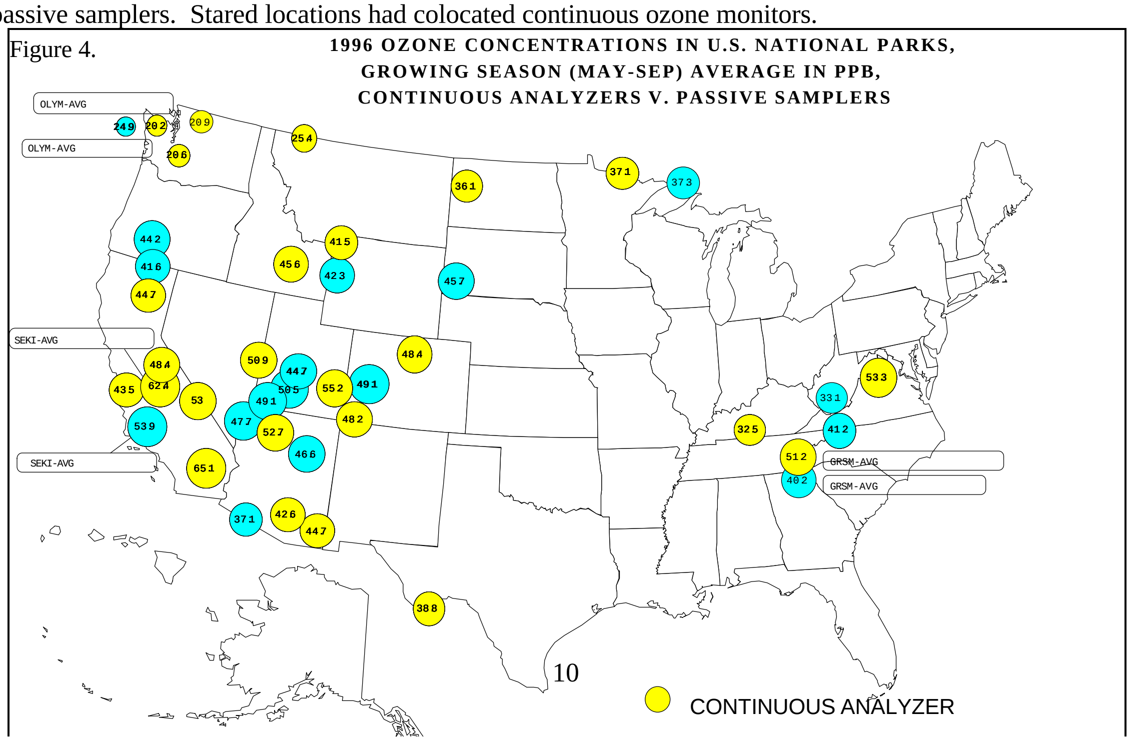


Figure 4. Map of the passive sampling locations in 1996 (shaded circles). The stared locations are nearby parks that have continuous ozone monitors. Large open circles are regional groups for comparing air quality data.

Comparison of Maximum Ozone Concentrations

Comparing the maximum weekly average ozone values between parks helps give an idea of the distribution of ozone between the different parks. The maps in Figures 5 and 6 have the maximum weekly ozone values plotted as proportional circles for 1995 and 1996 respectively. Grand Teton, Wind Cave, and Bryce Canyon parks had significantly higher maximum weekly concentrations in 1996 than in 1995. Blue Ridge Parkway had a higher maximum in 1995 than 1996. Very clean air was observed at the Olympic site 1. However, other sites within the park had higher ozone concentrations (see spatial distribution discussion). Parks that had maximum weekly averages above 70 ppb are likely to have had several days where the hourly ozone concentrations where in the 90-100 ppb range.

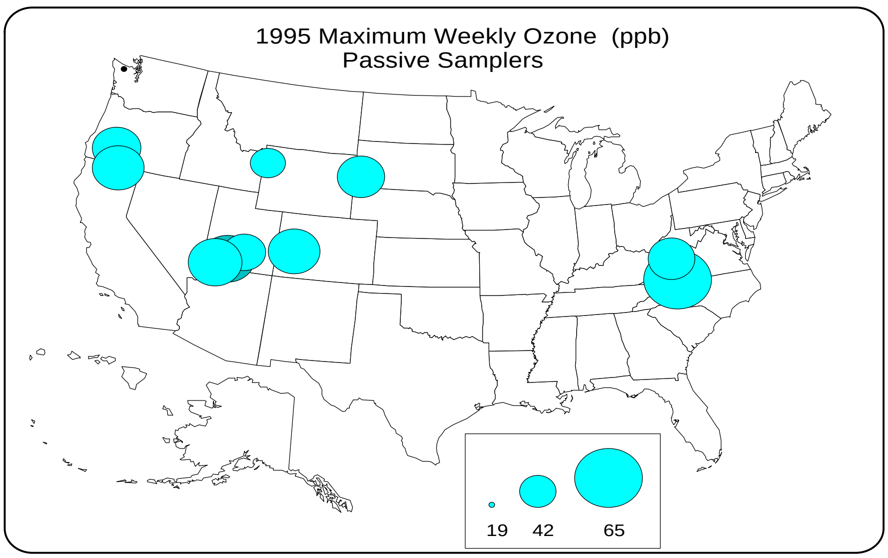


Figure 5. 1995 passive sampler ozone concentration maximums by park. Circles are proportional to concentration as indicated by the legend.

The sampler sites in parks relatively close together give some idea of how much variation can exist for a region. For example, the sites in the Colorado Plateau (BRCA, BLCA, CARE, ZION) have similar ozone values, but the California samples at Sequoia are much higher than the parks on the Colorado Plateau. The northern California and Oregon sites have similar ozone values, but the Olympic site is much lower. In the east, New River George tended to be cleaner that the higher elevation sites at Blue Ridge Parkway and

Great Smoky Mountains. The next closest park with ozone monitoring does not necessarily give a good estimate of ozone concentrations in the park of interest.

The timing of these maximum concentrations and a comparison to other continuous ozone monitors needs to be made to understand the events that led to these maximums. A later report will address that topic.

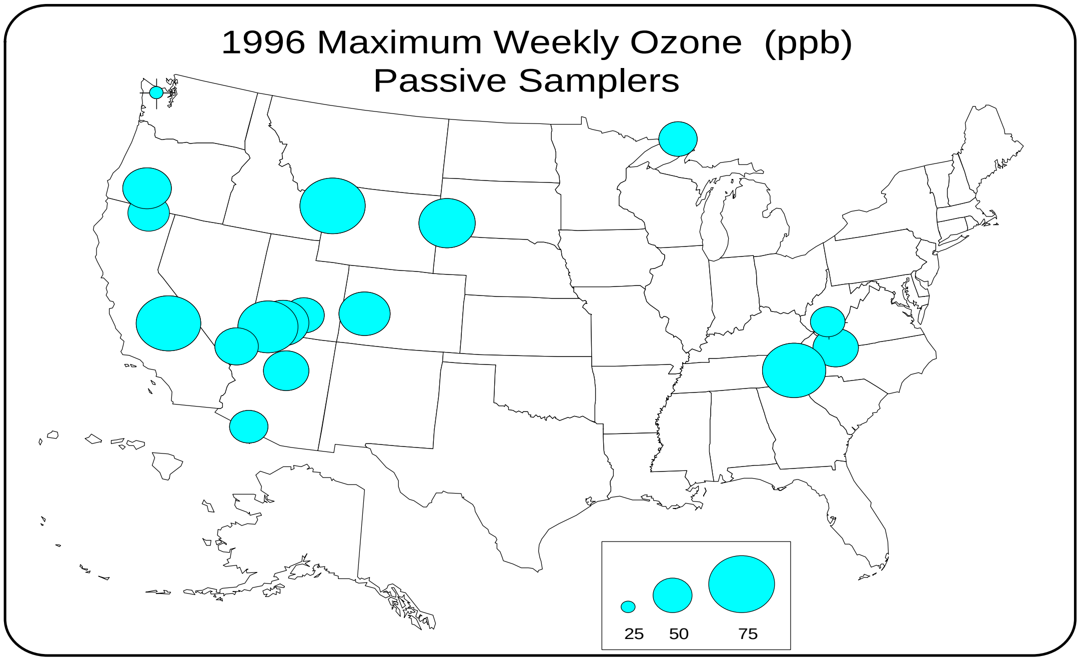
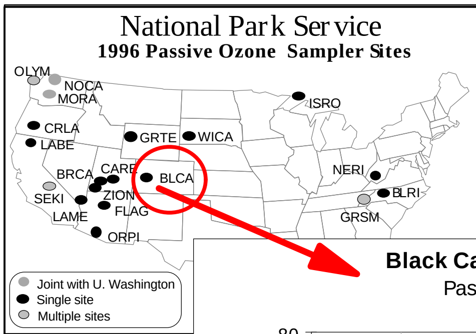


Figure 6. 1996 passive sampler ozone concentration maximums by park. Circles are proportional to concentration and can be estimated from the legand.

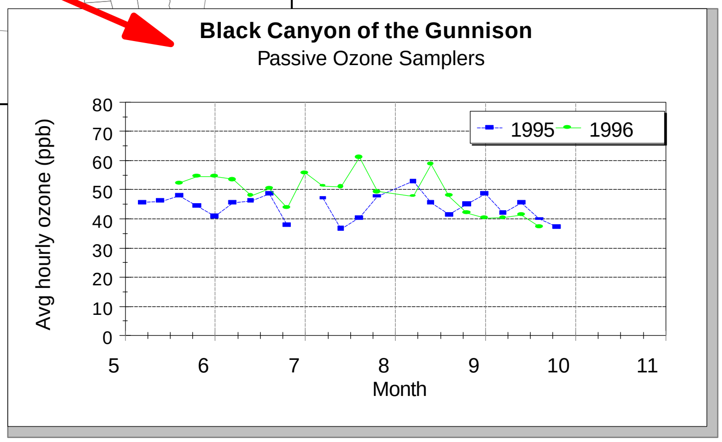
Graphical Summary Data by Park

Maps and data presented in this section are by regional groups as shown in Figure 4 and Table A5. Summary statistics in Table A5 allow comparison between years and other parks that are nearby. The parks are grouped according to areas that may have similar air sheds. All ozone concentrations are expressed as average hourly ozone in ppb units over the week-long sample exposure. Although the ozone data for the two years are often similar, they are not identical. The effects of weather systems on the ozone concentrations can be seen in several parks and in some cases two or three parks will have weekly ozone changes that are similar.



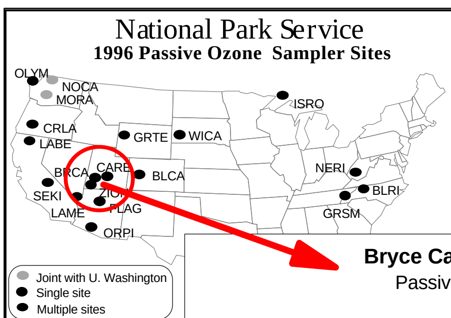
Average hourly ozone in ppb

	Avg	Std Dev	Max	Min
1995	44.2	4.1	53.0	36.6
1996	49.1	6.4	61.2	37.3



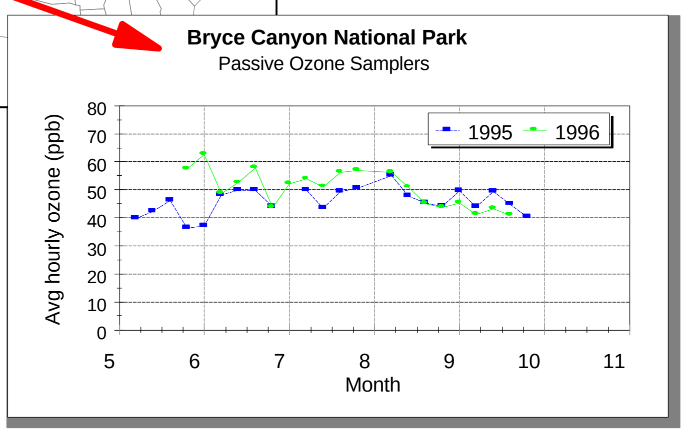
Although little seasonal variation is seen in weekly ozone concentrations at Black Canyon of the Gunnison, the ozone is elevated over what the background concentrations should be. Peak ozone values in 1996 were significantly above 1995 values.

Figure 7 Summary for Black Canyon of the Gunnision National Monument.



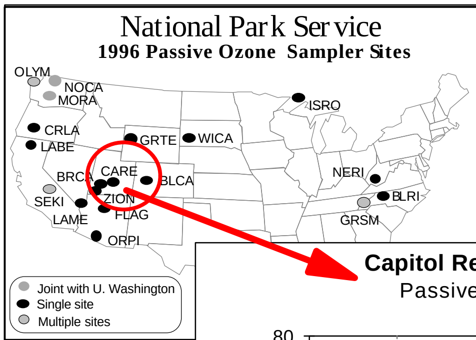
Average hourly ozone in ppb

	Avg	Std Dev	Max	Min
1995	45.8	4.6	55.2	36.5
1996	50.5	6.3	62.6	41.0



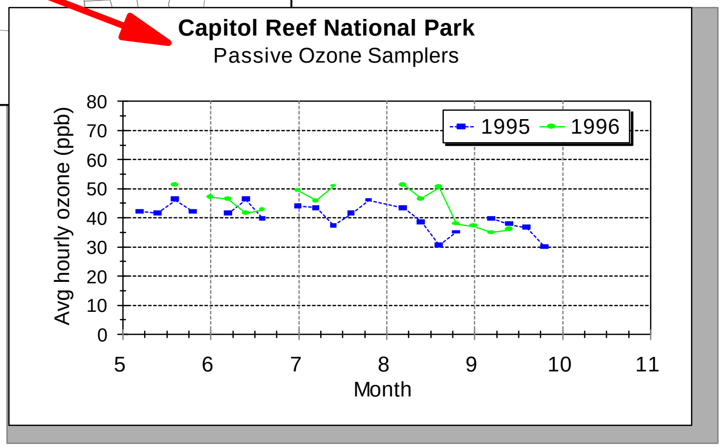
At Bryce National Park, ozone decreased slightly during the summer in 1996. The ozone peak in June was also observed at Zion NP. Ozone concentrations are elevated over the expected background and 1996 values were generally above 1995.

Figure 8 Summary for Bryce Canyon National Park.



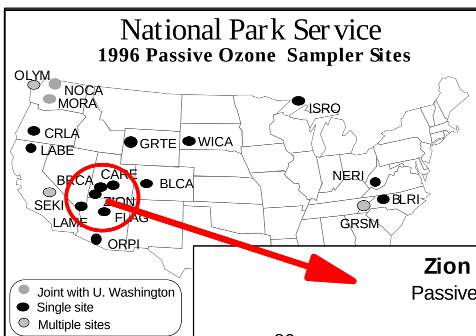
Average hourly ozone in ppb

	Avg	Std Dev	Max	Min
1995	40.2	4.5	46.2	30.0
1996	44.7	5.7	51.4	35.0



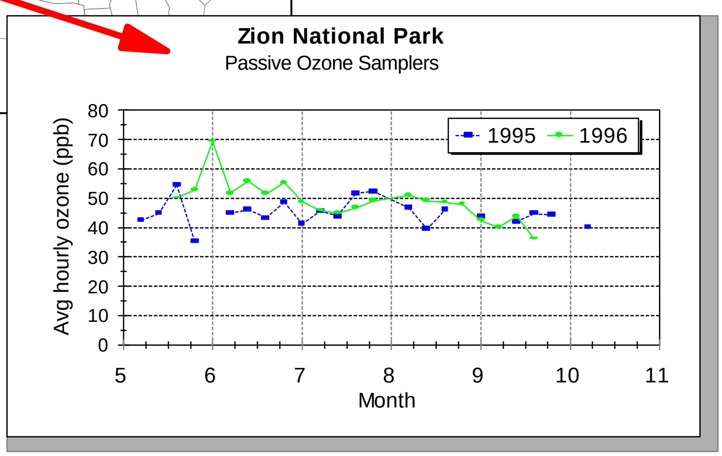
At Capitol Reef National Park, ozone decreases slightly during July and August in both 1995 and 1996. The ozone is elevated over what the background concentrations should be. Peak ozone values in 1996 were generally above 1995 values.

Figure 9 Summary for Capitol Reef National Park.



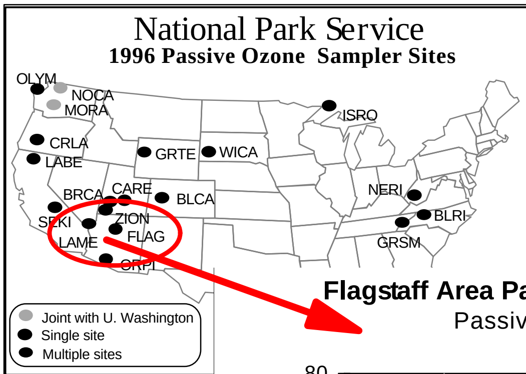
Average hourly ozone in ppb

	Avg	Std Dev	Max	Min
1995	44.9	4.3	54.6	35.3
1996	49.1	6.7	69.4	36.3

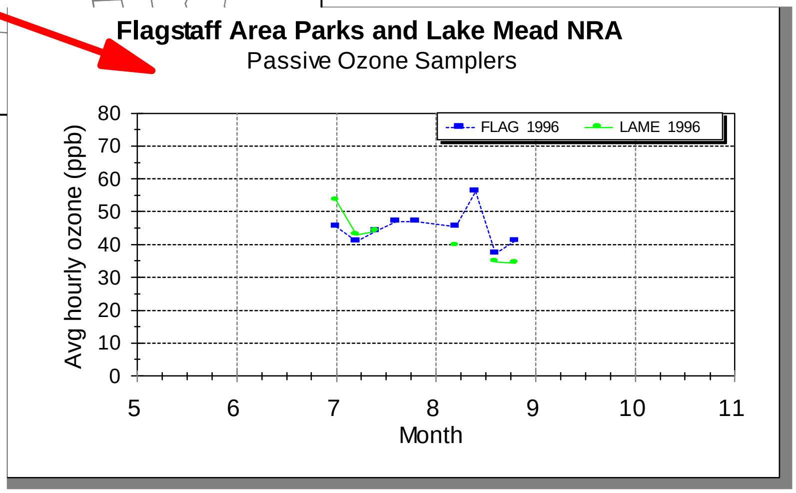


At Zion National Park, no seasonal change is observed in ozone in 1995 or 1996. The ozone is elevated over the expected background. The ozone spike in early June of 1996 may be an artifact.

Figure 10 Summary for Zion National Park.

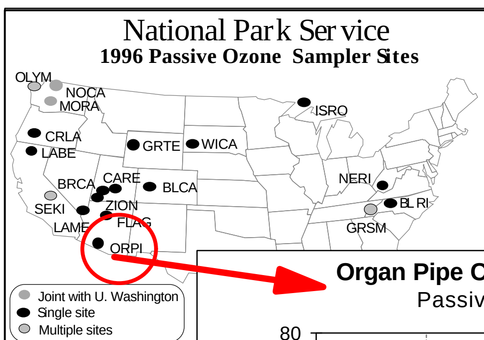


1996 Average hourly ozone in ppb	Avg	Std Dev	Max	Min
FLAG	44.9	5.0	56.2	37.3
LAME	54.7	3.6	63.2	50.9

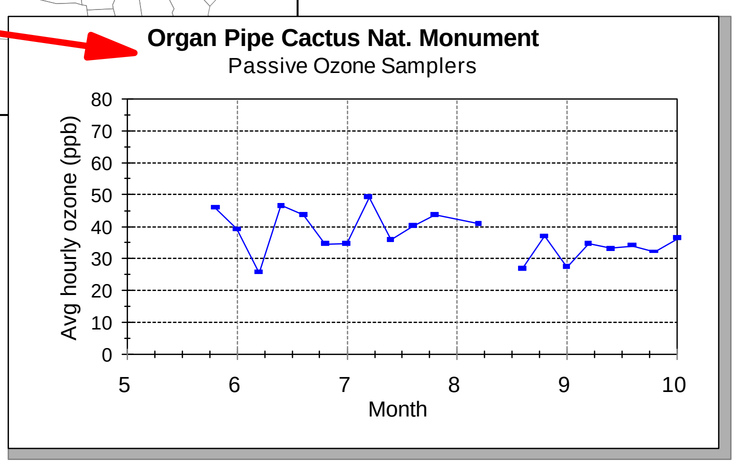


The Flagstaff area Parks and Lake Mead NRA had very semiliar ozone concentrations. See report for more detail on the spatial distribution with the parks and a comparison to other nearby parks.

Figure 11 Summary for Flagstaff area parks (Walnut Canyon, Sunset Crater Volcano, and Wapatki) and Lake Meade National Recreation Area.

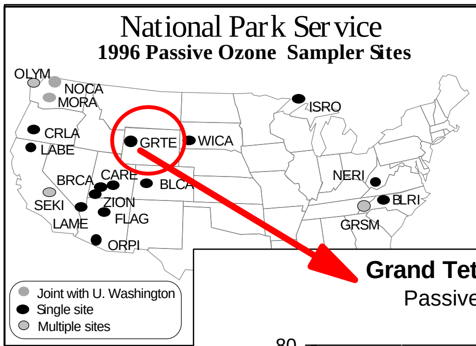


Average hourly ozone in ppb	Avg	Std Dev	Max	Min
1995				
1996	37.1	6.4	49.2	25.5



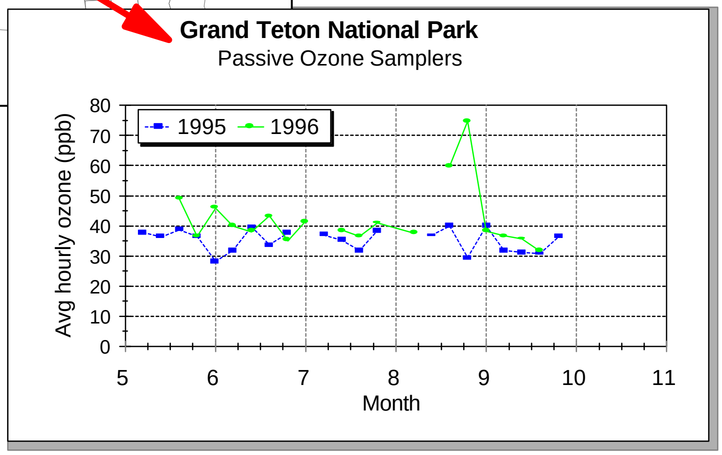
At Organ Pipe Cactus National Monument, ozone decreases slightly during July and August in 1996. The ozone is just slightly over the expected background concentrations for ozone. More weekly variation was observed in the spring than late summer.

Figure 12 Summary for Organ Pipe Cactus National Monument.



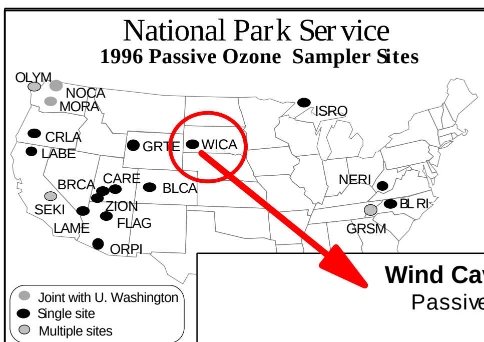
Average hourly ozone in ppb

	Avg	Std Dev	Max	Min
1995	45.3	3.5	40.0	28.3
1996	42.3	10.0	74.8	31.7



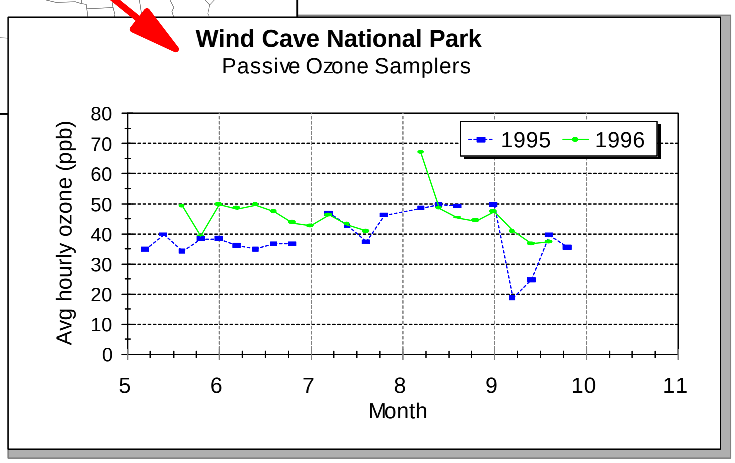
At Grand Teton National Park, no seasonal ozone trend is observed in either 1995 or 1996. The peak in August may be an artifact (see report text for more information). Little weekly variation is observed in ozone except for the August 1996 peak.

Figure 13 Summary for Grand Teton National Park.



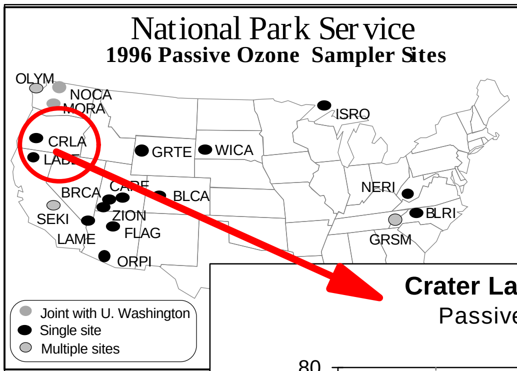
Average hourly ozone in ppb

	Avg	Std Dev	Max	Min
1995	39.0	7.7	49.8	18.7
1996	45.7	6.4	67.0	36.8



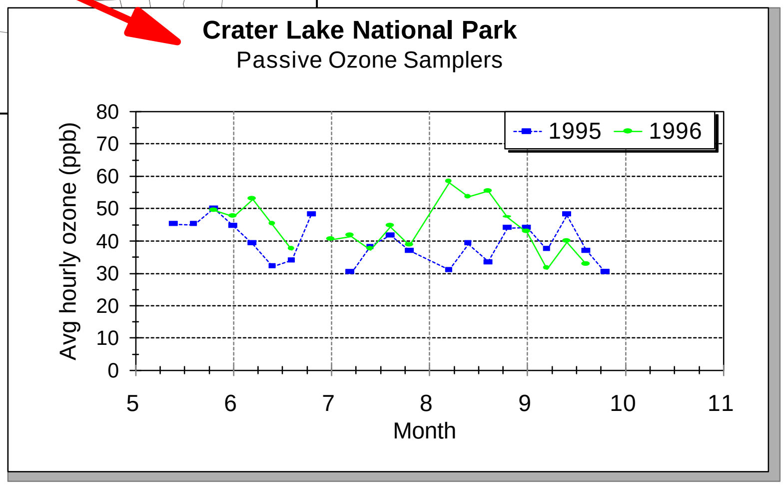
At Wind Cave National Park, ozone varied somewhat by week, but did not show a seasonal trend in either year. The August peak may be an artifact, the duplicate samples were not in good agreement. Spring had significant differences between years.

Figure 14 Summary for Wind Cave National Park.



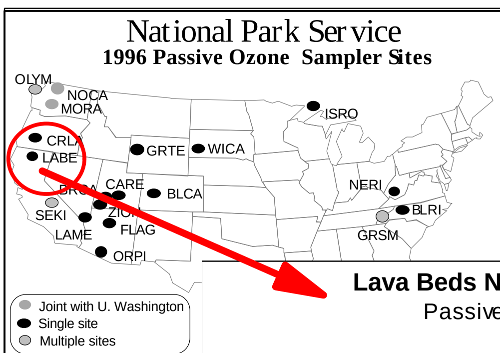
Average hourly ozone in ppb

	Avg	Std Dev	Max	Min
1995	39.6	6.1	50.2	30.2
1996	44.2	7.5	58.1	31.4



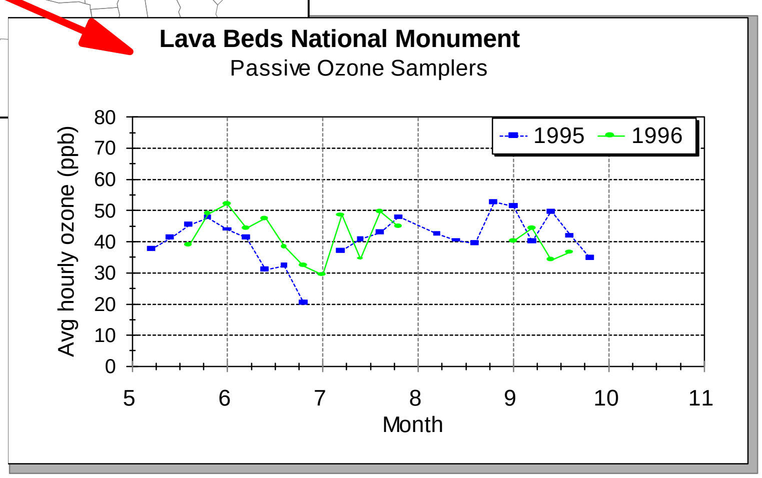
At Crater Lake National Park, significant week to week variation in ozone is observed. The air mass transport patterns need to be determined to explain the variations (see report text). 1996 peak ozone was significantly higher than in 1995.

Figure 15 Summary for Crater Lake National Park.



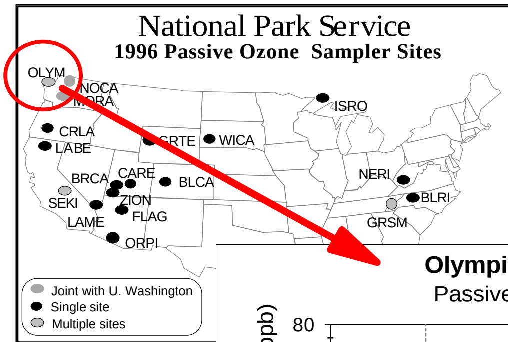
Average hourly ozone in ppb

	Avg	Std Dev	Max	Min
1995	41.1	7.1	52.9	20.5
1996	41.6	6.8	52.2	29.3



At Lava Beds National Monument, ozone is quite variable during the summer. The pattern of ozone change is similar to that observed at Crater Lake NP using passive samplers.

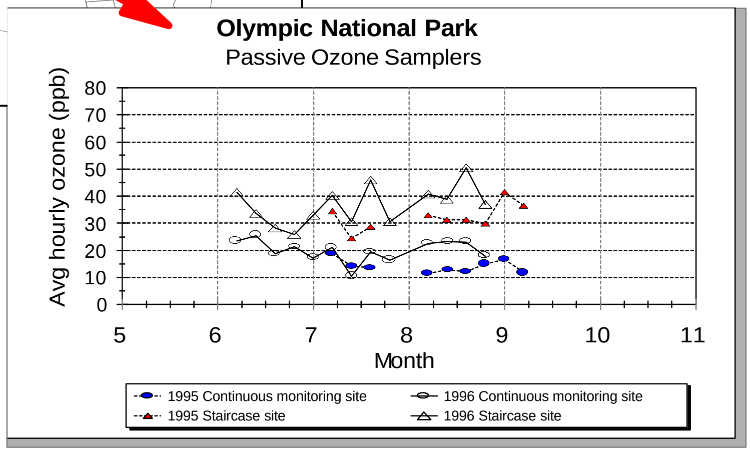
Figure 16 Summary for Lava Beds National Monument.



Average hourly ozone in ppb

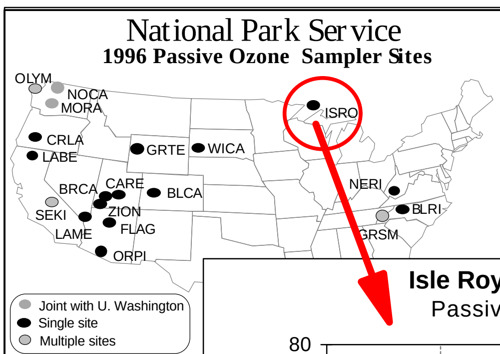
	Avg	Std Dev	Max	Min
1995	14.0	2.3	18.7	11.5
1996	20.0	3.8	25.5	10.4

⋆ Data for continuous monitoring site only



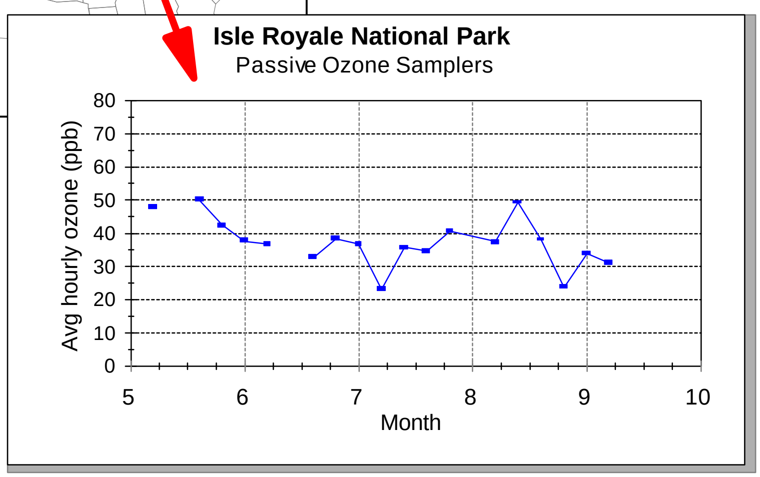
At Olympic National Park, ozone is generally quite low at the air quality monitoring station in Port Angeles. However, at Staircase the ozone concentrations are 2-3 times higher. Higher ozone values were observed in 1996. See report for O_3 spatial distibution.

Figure 17 Summary for Olympic National Park, continuous monitoring site and Staircase site in graph and continuous monitoring site only in data table.



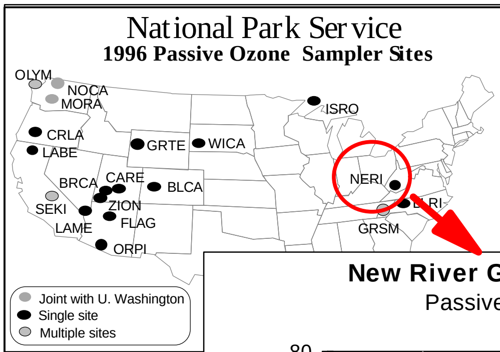
Average hourly ozone in ppb

	Avg	Std Dev	Max	Min
1995				
1996	37.3	7.2	50.4	23.2



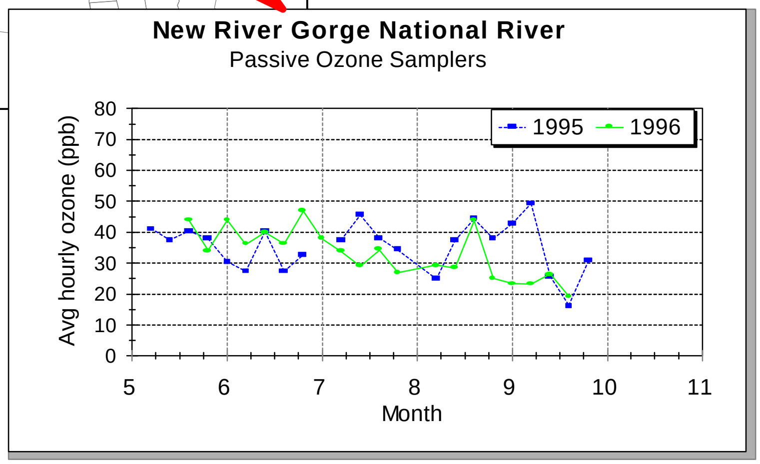
Isle Royale National Park had relately low ozone in 1996 with several weeks dropping to background ozone levels. The highest ozone concentrations were observed in spring and during one event in mid-August.

Figure 18 Summary for Isle Royale National Park.



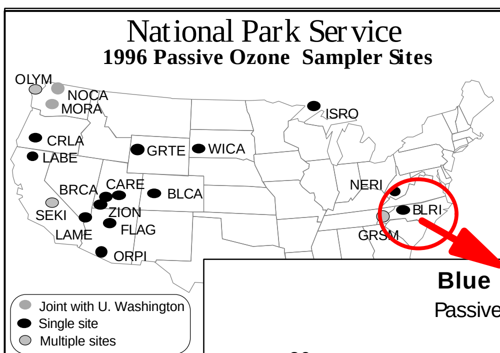
Average hourly ozone in ppb

	Avg	Std Dev	Max	Min
1995	35.4	7.7	49.3	16.4
1996	33.1	7.8	46.8	19.2



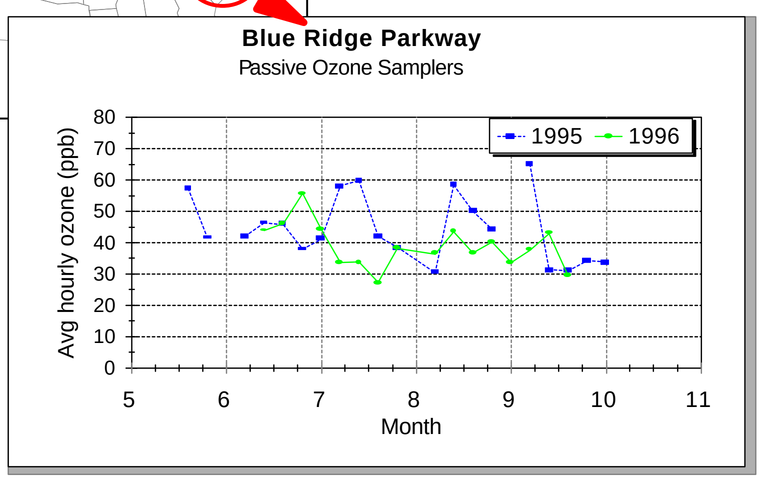
At New River Gorge National River, ozone decreased slightly during the summer, but also showed weather related events. For an Eastern site, the average ozone concentrations are low. The differences between years for average and maximum are minor.

Figure 19 Summary for New River Gorge National River.



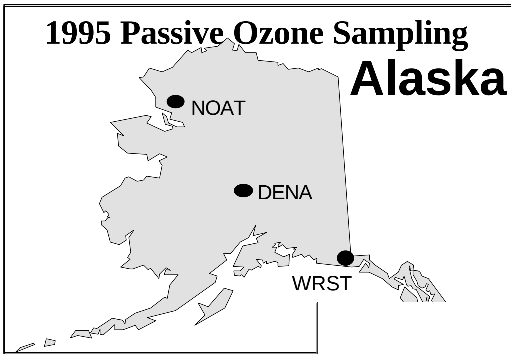
Average hourly ozone in ppb

	Avg	Std Dev	Max	Min
1995	44.5	10.3	65.1	30.4
1996	39.0	6.8	55.7	27.3



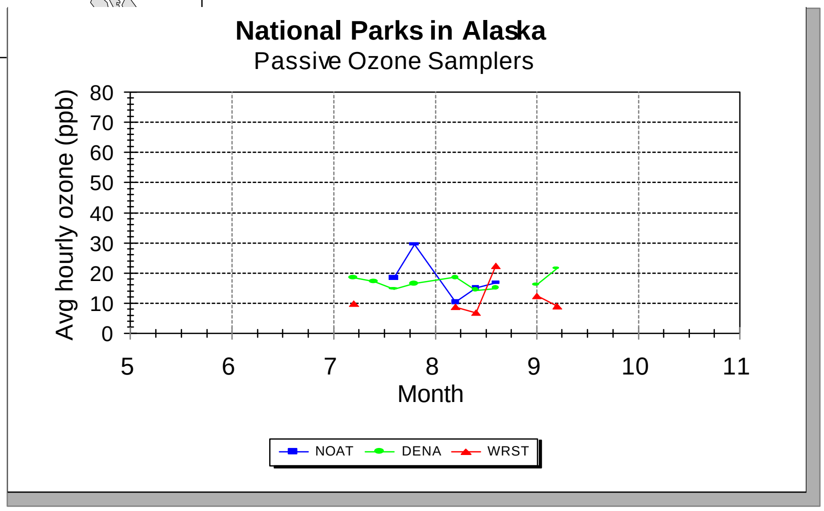
At Blue Ridge Parkway, a series of high ozone events was observed in 1995 but not repeated in 1996. Ozone is elevated over what the background concentrations should be. Peak ozone values in 1995 were significantly above 1996 values.

Figure 20 Summary for Blue Ridge Parkway.



Average hourly ozone in ppb

	Avg	Std Dev	Max	Min
DENA	16.9	2.2	21.5	14.3
NOAT	18.1	6.3	29.5	10.4
WRST	11.6	5.1	22.4	6.9



The three National Parks in Alaska that sampled for ozone in 1995 had very similar ozone concentrations that were quite low.

Based on ozone concentration, the Alaskan parks have excellent air quality during the summer.

Figure 21 Summary of passive ozone for 1995 in three National Parks in Alaska.

Comparison of Ozone between Parks

Colorado Plateau Parks

A number of passive sampling locations were on the Colorado Plateau, which provides an opportunity to compare the ozone concentrations over a region where the NPS has several continuous ozone monitors. The region is thought to have relatively clean air, although visibility studies for the Grand Canyon have shown that pollution can be transported hundreds of miles from urban and industrial areas to the region. To what extent can the existing continuous monitoring stations be used to represent the ozone concentrations at other parks on the Colorado Plateau?

The weekly plots of ozone for the Colorado Plateau parks in the previous section illustrates several points. A weather-related pattern is seen with fairly constant ozone in May and June, a rapid drop in the second week of July, and then an increase to the summer maximum in July-August. The parks obtain their August high ozone with different lag times from the low in the second week of July (Figure 21). Both Mesa Verde and Grand Canyon have higher ozone concentrations than the other Colorado Plateau parks. Elevation and location along the Colorado River drainage may influence the ozone concentrations.

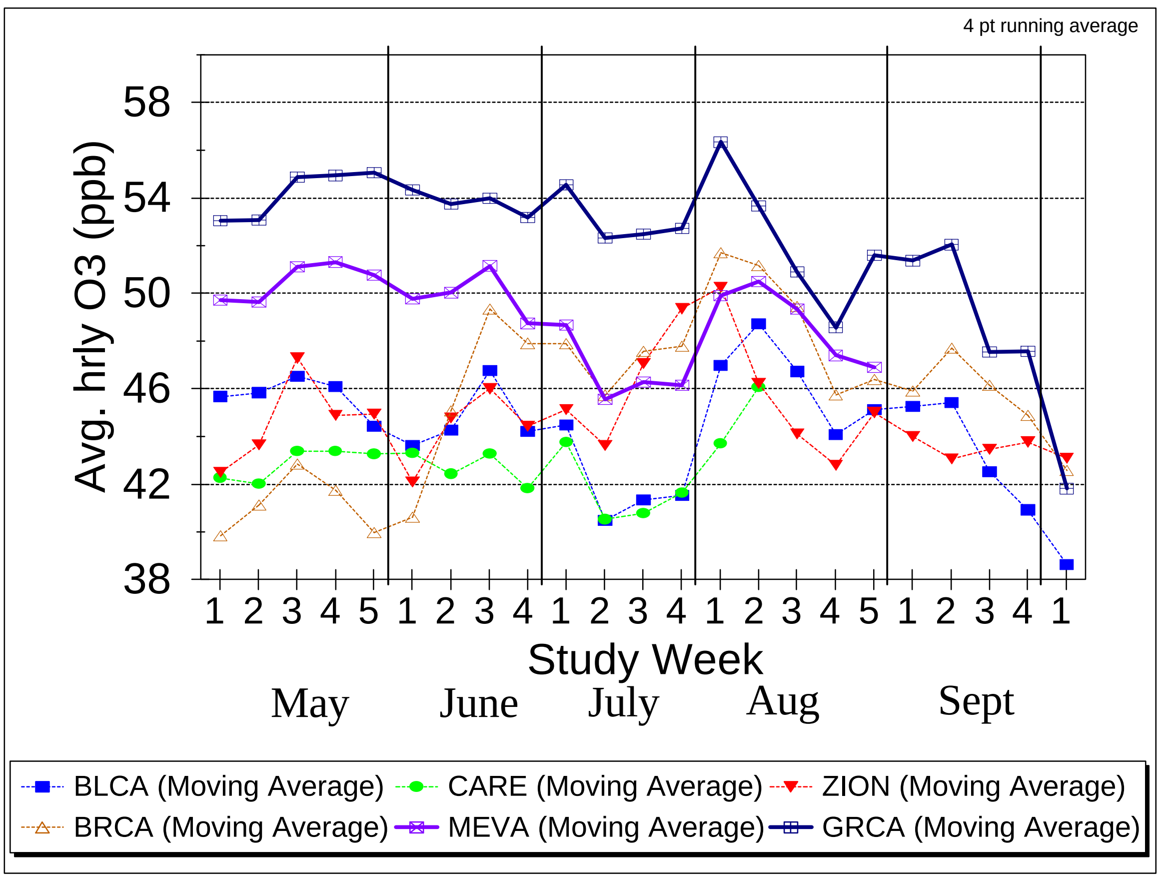


Figure 22 Time series plot for weekly average ozone concentrations for parks on the Colorado Plateau. GRCA, MEVA, BLCA, and CARE are along the Colorado River drainage and have a similar time series pattern.

Table II. **Comparison of 1995 average hourly ozone for the weekly samples**

Month	Week	Index Wk	Passive Black Canyon of the Gunnison	Avg O3 Mesa Verde	Max Hourly O3 Mesa Verde	Passive Capitol Reef	Avg O3 Canyonlands	Max Hourly O3 Canyonlands	Passive Bryce Canyon	Passive Zion	Avg O3 Grand Canyon	Max Hourly O3 Grand Canyon	Avg O3 Great Basin	Max Hourly O3 Great Basin
5	1	1	45.7	50.6	61	42.3	48.8	63	39.8	42.5	54.9	75	45.1	63
5	2	2	46.0	48.1	60	41.7	48.8	62	42.4	44.8	52.1	68	48.1	57
5	3	3	47.9	56.0	66	46.1	51.2	66	46.3	54.6	58.7	73	49.4	79
5	4	4	44.4	50.3	67	42.3	49.7	61	36.5	35.3	52.8	69	41.3	53
5	5	5	41.0	47.9	67	41.3	46.5	65	37.1	44.9	53.8	69	42.8	64
6	1	6	45.5	51.4	71	46.2	46.4	61	48.2	46.0	55.2	68	48.2	73
6	2	7	46.3	51.7	67	39.7	49.2	65	49.9	43.4	53.8	75	45.8	70
6	3	8	48.5	48.1	60	43.9	48.6	65	49.9	48.5	54.3	72	43.2	69
6	4	9	37.8				.	.	43.9	41.3	.	.	.	.
7	1	10	47.1	49.8	67	43.5	49.4	62	49.9	45.5	52.3	67	48.1	60
7	2	11	36.6	41.5	56	37.5	47.6	73	43.4	44.0	48.8	65	47.8	58
7	3	12	40.3	46.0	56	41.3	46.4	58	49.3	51.6	55.2	73	48.6	61
7	4	13	47.7	52.0	63	46.1	54.9	81	50.6	52.4	58.0	69	49.3	69
8	1	14	53.0	53.2	68		51.7	65	55.2	46.8	58.3	71	51.0	76
8	2	15	45.5	47.9	68		48.5	60	47.8	39.5	46.2	59	50.7	70
8	3	16	41.7	46.9	68		48.2	58	45.4	46.0	48.2	57	42.7	57
8	4	17	45.0				47.5	59	44.1		51.3	62	44.2	61
8	5	18	48.7				50.6	66	49.6	44.0	55.3	73	50.7	62
9	1	19	42.0			30.0	52.5	88	44.0		47.5	58	47.2	64
9	2	20	45.5				42.7	57	49.5	42.1	53.3	61	46.2	62
9	3	21	40.0				41.4	53	45.0	44.8	41.8	68	45.5	64
9	4	22	37.3			37.8	.	.	40.2	44.4	.	.	.	.
10	1	23				36.5	.	.		40.0	.	.	.	.
Mean			44.2	49.4		41.1	48.5		45.8	44.9	52.6		46.8	
Maximum			53.0	56.0	71	46.2	54.9	88	55.2	54.6	58.7	75	51.0	79

Based on the correlation matrix, the following parks have similar ozone concentration patterns:

1. GRCA - with MEVE, CARE, ZION
2. MEVE - with GRCA, CARE, and BLCA
3. ZION - with BRCA
4. CARE - with BLCA, MEVE

Table III. Correlation matrix for Ozone concentrations in Colorado Plateau parks.

Variable	**lack Canyon**	**Mesa Verde**	**Capitol Reef**	**Canyon lands**	**Bryce Canyon**	**Zion**	**Grand Canyon**	**Great Basin**
Black Canyon	1.000							
Mesa Verde	0.798	1.000						
Capitol Reef	0.728	0.744	1.000					
Canyon lands	0.568	0.534	0.458	1.000				
Bryce Canyon	0.377	0.172	0.332	0.255	1.000			
Zion	0.217	0.246	0.477	0.292	0.643	1.000		
Grand Canyon	0.581	0.787	0.787	0.493	0.324	0.649	1.000	
Great Basin	0.049	0.118	0.261	0.256	0.604	0.684	0.271	1.000

Looking at a topographical map, one can see that MEVE, BLCA, GRCA, and CARE are in or along the Colorado River drainage, while Zion and Bryce Canyon are on a plateau on the northwest side of a mountain range and above the Colorado River drainage. The correlation matrix in Table III provides another estimate of which parks have similar ozone pollution on a weekly basis. Even parks close to each other (Zion and Bryce Canyon) do not have large correlations. However, their average seasonal ozone concentrations are close. Thus, we conclude that the two nearest continuous ozone monitoring stations at Grand Canyon and Mesa Verde, are an imperfect representative for ozone concentrations at Zion and Bryce Canyon National Parks. In general, Grand Canyon has higher average ozone and maximum ozone concentrations than the other Colorado Plateau parks.

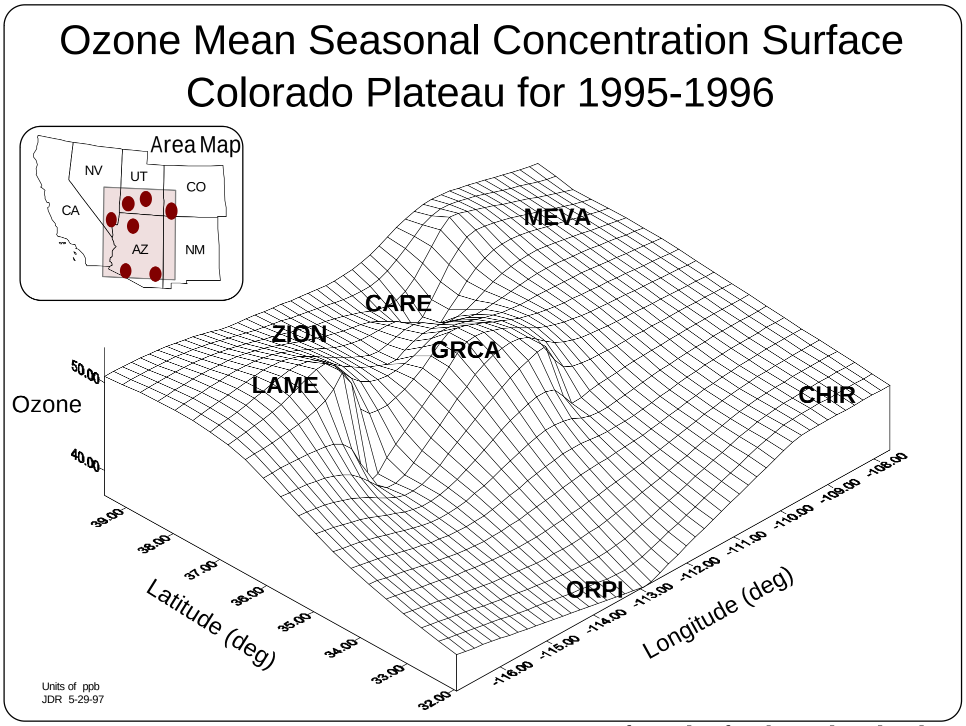


Figure 23 Mean ozone concentrations are given a 3-D surface plot for the Colorado Plateau to show the regional variations. The hatched area on the inset map shows the approximate area covered by the surface plot. The markers on the inset map correspond to the park codes on the surface plot.

The 3-D surface plot for average ozone concentrations in the Colorado Plateau region (figure 23) gives an interesting view. The surface plot suggests that the region does not have uniform ozone concentrations. Higher ozone regions can be explained by either transport from more polluted areas or by relatively local ozone production. The high ozone peaks around Lake Mead and Grand Canyon look like local ozone production may be an influence. For this region the expected background ozone concentration is about 35 ppb based on computer models (Jacob et al, 1993) or between 26 to 46 ppb based on measurements at other inland western sites (Altshuller and Lefohn, 1996). Thus, most of the Colorado Plateau region is above the expected background ozone concentrations.

Although overall average ozone concentration may have some influence on human health and plant damage, most experts believe that high 1-hour maximum ozone concentrations relate better to human health problems or plant injury. The continuous analyzer data can help classify the diurnal variability and the expected maximum 1-hour concentrations for the region. The table below compares the maximum 1-hour ozone concentrations for summer by park and year. Only Saguaro NM has maximum hourly ozone values approaching the National Standard of 120 ppb.

Table IV. Maximum 1-hour ozone concentrations observed at Colorado Plateau NPS units.

Park	**88**	**89**	**90**	**91**	**92**	**93**	**94**	**95**	**96**
ARCH	70	80	56	74					
CANY					65	75	73	88	82
COLO	69	67	70	72					
MEVE						67	72	71	77
GRCA		68	74	79	78	73	79	75	84
GRBA						63	75	79	81
CHIR								81	80
SAGU	100	99	103	96	104	102	109	118	92

Ozone Spatial Distributions

The question here is similar to that posed in the last section except on a more immediate distance scale. To what extent is the data from a single continuous ozone monitoring station in a park representative of the ozone concentrations throughout that park? This question is important for taking the vegetation injury data that is available and trying to estimate the extent of vegetation injury that might occur within a park. These studies looked at the variation in ozone concentrations based on geographical location.

Multiple sample locations have been used in a number of parks to determine how ozone is distributed in complex terrain. The parks chosen for these studies generally have high ozone concentrations and, often, some on-going ozone injury effects studies. Great Smoky Mountains, Rocky Mountain, and Sequoia-Kings Canyon National Parks were used in the initial testing of the passive samples and were chosen for spatial studies. Mount Rainier, Olympic, and North Cascades studies were done cooperatively with Dr. David Peterson at the University of Washington. Separate reports on those studies have been prepared by Dave Peterson and Sarah Brace (Brace, 1996). This report provides the ozone values currently available and examples from the Great Smoky Mountains and Rocky Mountain National Park studies.

The brief examples presented in this section illustrate the following points:

- Over a distance of 10-15 miles, especially in complex terrain, ozone concentrations can vary by factors of two to three.

- Often, but not always, ozone concentrations increase with elevation. High-elevation sites are more likely to see fairly consistent ozone concentrations without the strong diurnal variation that is observed in urban areas.

- Polluted air containing ozone is transported up drainages and distributed unevenly within a park (for example, transport from the front range of Colorado to the eastern side of Rocky Mountain NP or the transport of air with high ozone from the San Joaquin Valley to the western side of Sequoia-Kings Canyon NP).

- The high spatial variability of ozone within a park makes it even more unlikely that urban or suburban monitoring stations will be representative of the air quality in a park that is some distance away and in mountainous terrain.

Blue Ridge Parkway Study

Three locations along the Blue Ridge Parkway were chosen to measure ozone using the passive sampler. In this spatial distribution study, the sites with linear north-south and all along the ridge line of the parkway.

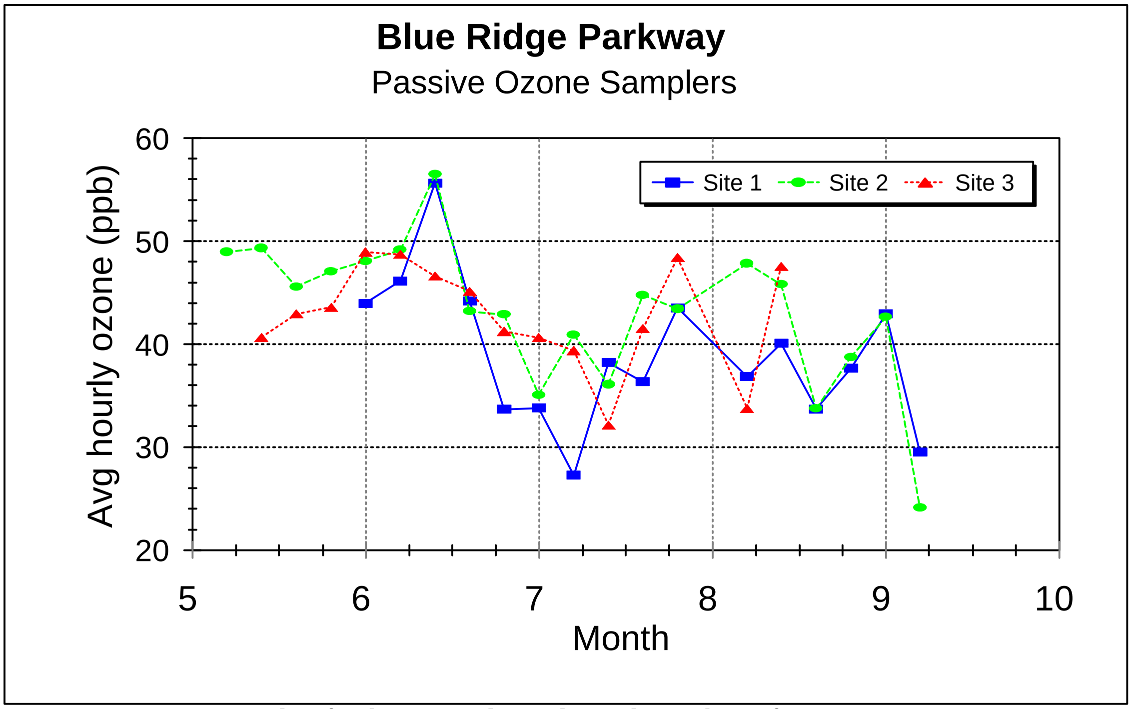


Figure 24 Ozone data for three sites along Blue Ridge Parkway for summer, 1996.

Table V Statistical Summary on Ozone for the Blue Ridge Parkway, 1996

Location	Mean	Std Dev	Max	Min
1	39.0	6.8	55.7	27.3
2	43.2	6.9	56.5	24.1
3	41.1	8.1	49.0	15.6

The ozone concentrations observed at the sampling sites on the Blue Ridge Parkway were similar in magnitude and in temporial variability during the summer. A period corresponding to clean air was observed in early- to mid-July at all three sites. A similar decrease in ozone was observed at the same time at the Cove Mountain monitoring station in Great Smoky Mountains NP. This corresponded to the passage of hurricane Bertha that made landfall in southern North Carolina and proceeded up the eastern coast. In early September, a second hurricane, Fran, made landfall at nearly the same place and proceeded north through North Carolina and Virginia. Ozone concentrations decreased significantly during that period also along the Blue Ridge Parkway.

Olympic National Park Study

In this study, six locations were sampled weekly along the eastern edge of Olympic National Park. Three sites going up Hurricane Ridge were chosen to look for an elevation gradient in ozone concentrations and three more sites on the eastern edge of the park were chosen to look for the effects of local air pollution transport from the Seattle area. Since the NPS air quality station is at low elevation and to the north of the park, the question of how representative the continuous ozone monitoring site is to the rest of the park must be asked. Data for Mt. Rainier NP indicates an elevation gradient in ozone that means park natural resources are exposed to higher ozone concentrations than indicated by the monitoring station. The passive ozone samplers allow us to answer that question.

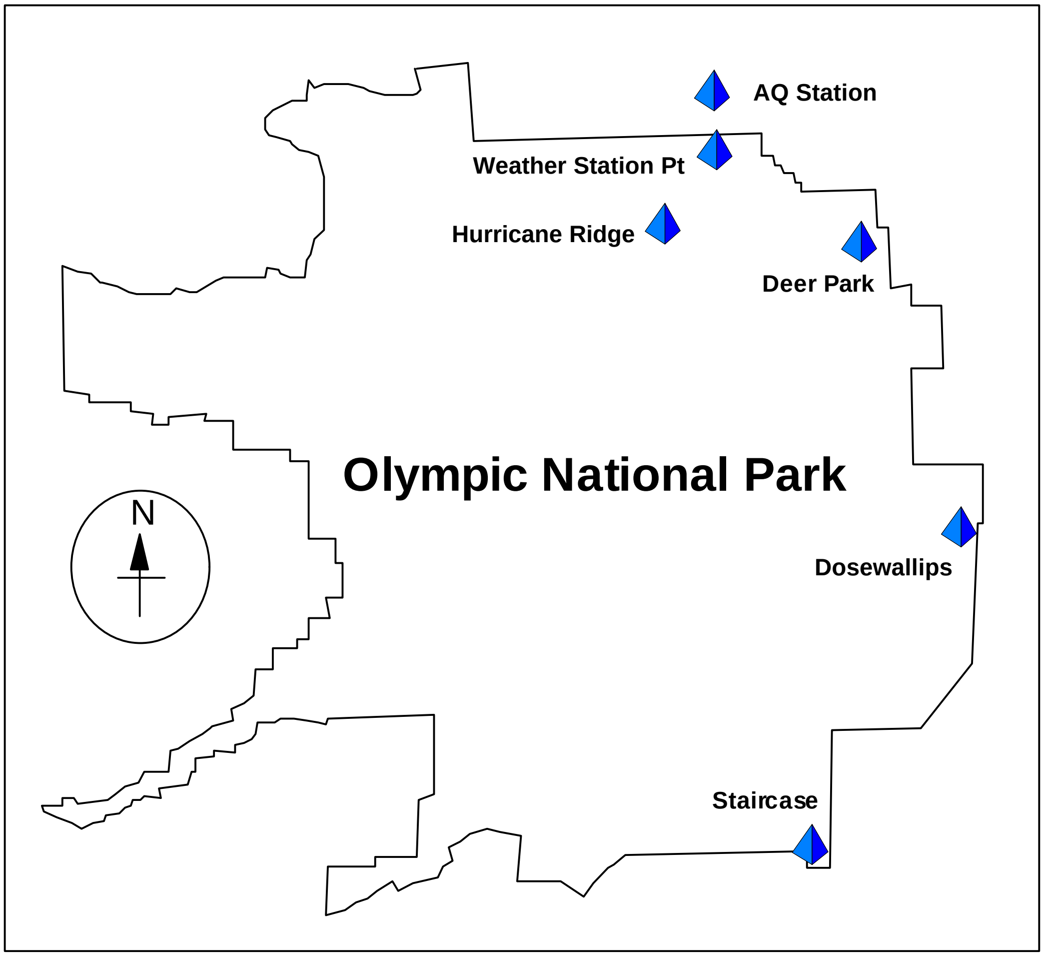


Figure 25 Map of Olympic National Park with the locations of the passive ozone monitoring stations indicated.

The data for 1996 shows weather induced variations in ozone during the summer months and the highest weekly ozone in August. There are significant differences between the ozone at the different monitoring sites that are fairly consistent for the season. Table VI gives some statistical values that quantify these differences. The mean ozone values for Olympic NP are well below what we have observed at most other Parks.

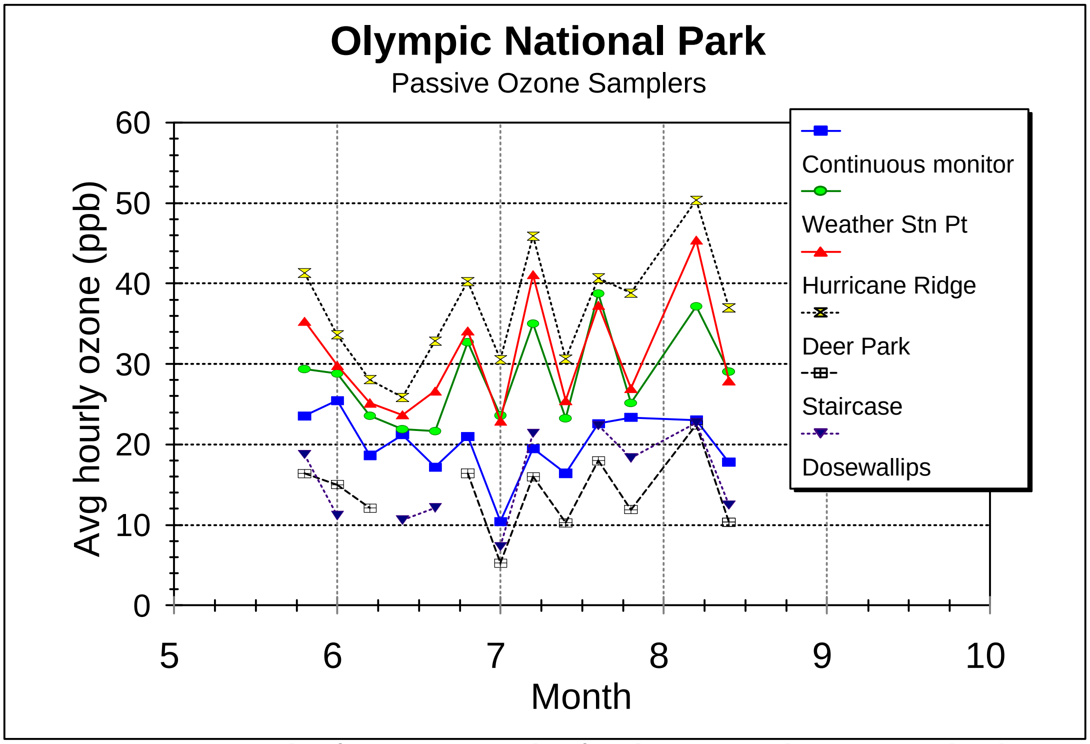


Figure 26 1996 ozone data from passive samplers for 6 locations in Olympic National Park.

Table VI Statistical Summary for Olympic National Park, 1996

Location	Mean	Std Dev	Max	Min
Continuous monitoring site	20.0	3.8	25.5	10.4
Weather Station Point	28.5	5.7	38.7	21.6
Hurricane Ridge	30.9	6.8	45.4	23.0
Deer Park	36.6	6.9	50.4	25.9
Staircase	14.0	4.4	22.5	5.3
Dosewallips	12.8	8.3	22.8	0

At Olympic National Park, the ozone concentrations increase with elevation for sampling sites in the northern section of the park. The difference between the lowest ozone site and the highest ozone site is about a factor of three. The continuous ozone monitoring station has a season mean that is about midway between the highest and lowest. Thus, although the measurements at the current location of the continuous ozone monitor are not representative of all the park, it does give something close to an average value.

The ozone gradient with elevation is an interesting feature. Figure 27 shows the passive sampler data plotted for 1995 by elevation (in feet above sea level) of the site. A linear regression yields the relationship:

Ozone (ppb) = 8.86 + 0.00373 * (elevation) $R^2 = 0.725$

Thus, ozone increases by 3.7 ppb per 1000 feet. Compare this equation with the gradient seen at Mt Rainier NP of 3.3 ppb per 1000 feet (Brace, 1996):

Ozone (ppb) = 11 + 0.0033 * (elevation)

Or to the 12.6 ppb per 1000 feet ozone gradient observed at Great Smoky Mountains NP in 1994 where 26 sampling locations were used over a three-week period in the summer.

Ozone (ppb) = -1.6 + 0.0126 * (elevation) $R^2 = 0.707$

Great Smoky Mountains NP has a much higher average ozone (~54 ppb) and maximum hourly ozone concentrations nearer the National Standard of 120 ppb. It appears that the gradient is a function of the overall pollution levels in the region.

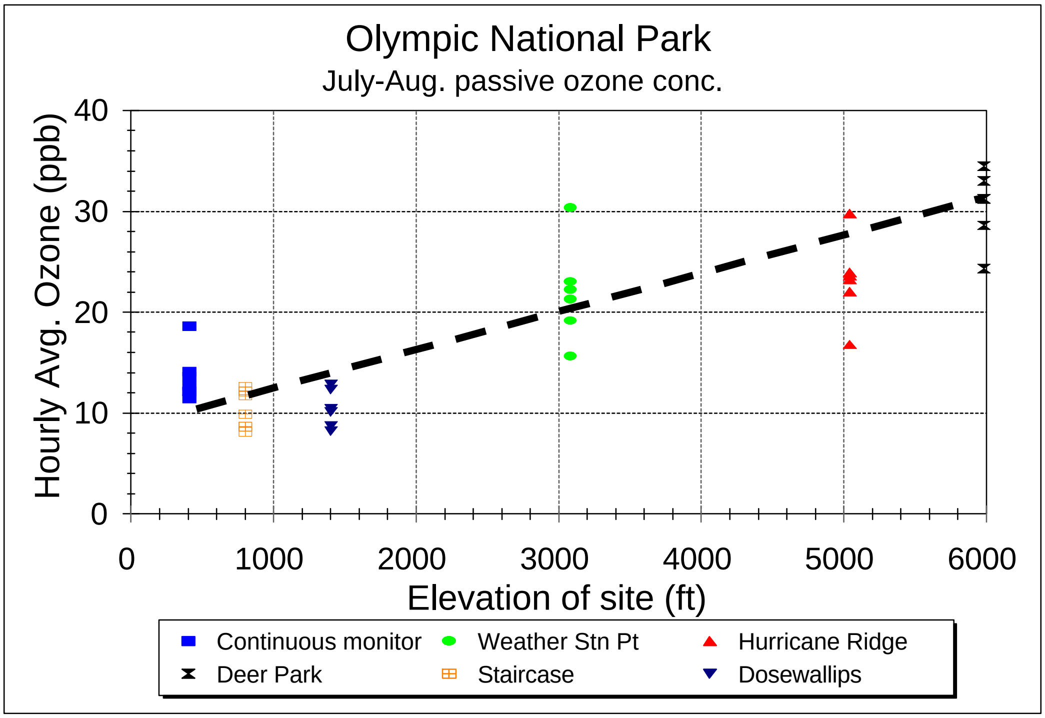


Figure 27   1995 ozone data from passive samplers for 6 locations in Olympic National Park. The heavy dashed line is the linear regression fit for the data.

Some additional work should be done with this data to develop an ozone contour map for the eastern side of the park. A map overlay with plots of sensitive species would then give indicators of areas where the vegetation might be at greater risk to ozone induced plant injury. Additional sampling sites are planned in 1997 on the west side of the park.

Sequoia-Kings Canyon National Park Study

This study looked at seven locations widely spaced within the park as a preliminary to a larger study where more than 20 sites would be used. The three continuous ozone monitoring stations in the Park are located along the southwestern edge and are used for comparison to the passive samplers.

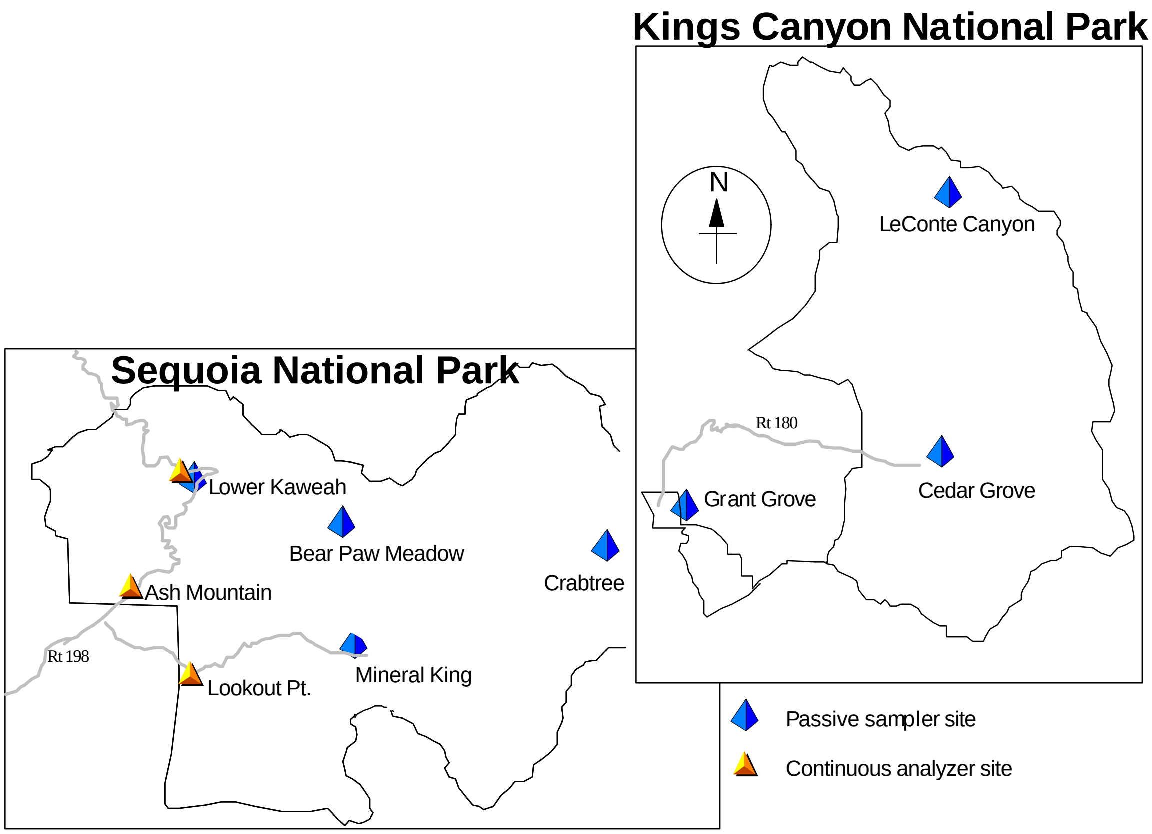


Figure 28a Maps indicating the approximate locations of ozone monitoring in the parks.

Table VII Statistical Summary for Ozone at Sequoia-Kings Canyon, 1996

Location	Mean	Std Dev	Max	Min
Crabtree	48.4	4.6	57.5	40.2
LeConte Canyon	49.0	5.2	56.6	40.1
Bear Paw Meadow	62.8	7.4	71.1	44.1
Mineral King	51.3	16.3	68.8	29.7
Cedar Grove	39.4	5.5	46.6	27.4
Lower Kaweah	64.6	7.8	74.4	45.7
Grant Grove	59.0	8.3	69.5	44.6

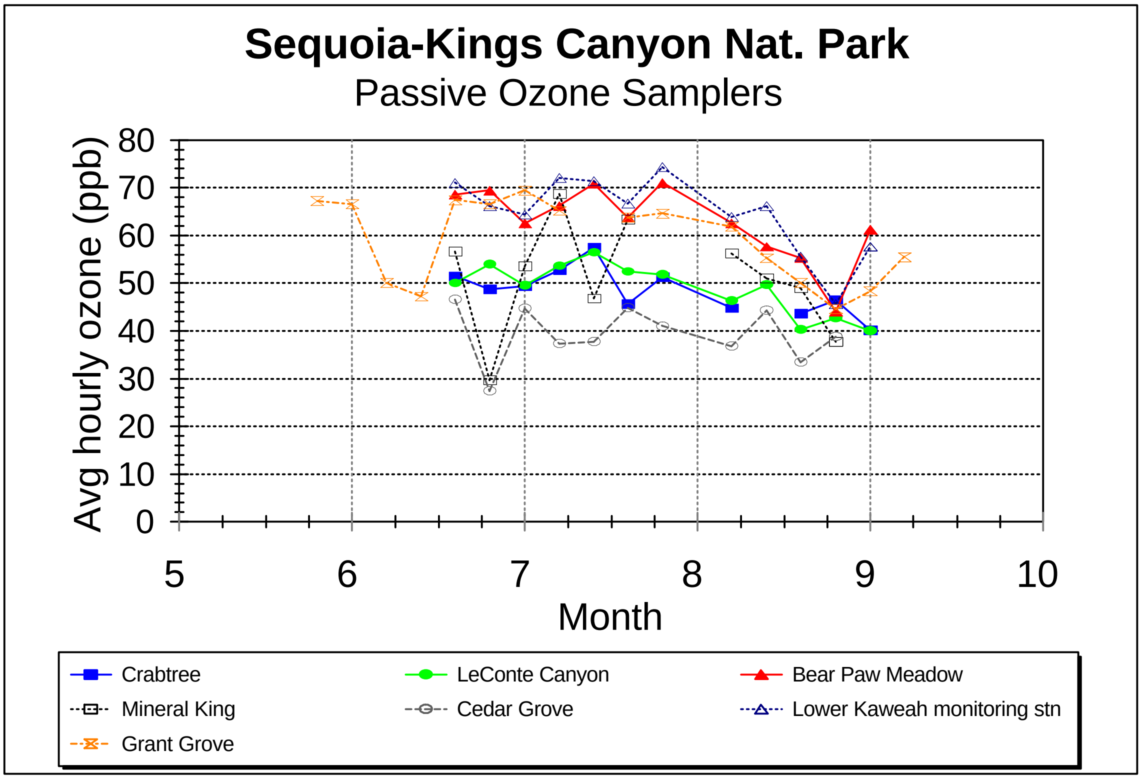


Figure 28b Plots of the ozone concentrations at 7 sites indicate a wide range in concentrations.

The Lower Kaweah ozone monitoring station records several high ozone-events above the National Standard (NAAQS) of 120 ppb each year. Crabtree (10, 700 ft) and LeConte Canyon (8,700 ft), on the east side of the parks, and Cedar Grove (4,700 ft) are interior locations that receive less ozone pollution. Data from Bear Paw (7,800 ft), Mineral King (7,500 ft), and Grant Grove (4,700 ft) indicate that polluted air from the San Joaquin Valley that is observed at Lower Keweah is also affecting these other sites. The Lower Kaweah station recorded the highest ozone concentrations of all the sampling locations. Since Bear Paw and Grant Grove have nearly as high of ozone values and follow the same weekly pattern as Lower Kaweah (see Figure 28b), it is likely that these areas are also having exceedances of the NAAQS standard. Although the difference between sites is seen for most of the summer, during late August the ozone concentrations were nearly the same for all the sites. The relatively clean air during that period indicates a disruption of the normal air mass flow from the west that brings polluted air. This small study shows that Sequoia-Kings Canyon NP has a wide variation in ozone exposures within the park and that the larger study would be very useful in mapping out the areas of the park that are most at risk to this air pollution.

Rocky Mountain National Park Study

The spatial distribution study at Rocky Mountain NP was one of the first to be done with passive samplers. Nine locations within Rocky Mountain National Park were sampled for ozone over a three-week period.

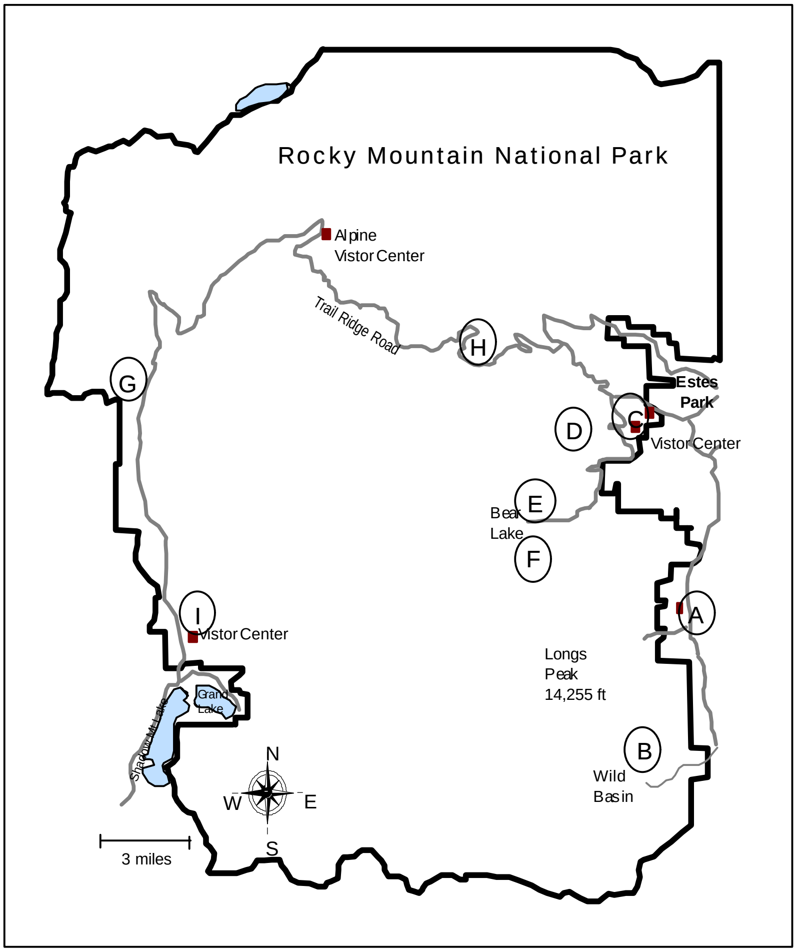


Figure 29 Map of Rocky Mountain National Park with the passive sampling sites indicated.

All of the results in Figure 30 are referenced relative to the ozone concentrations observed at the air monitoring station on the east side of Long's Peak (labeled site **A** in Figure 29). Because of the short duration of the study, it is not known if the observed patterns are valid for the whole of the ozone season (May through September). However, clear differences between the east and west sides of the Park were observed.

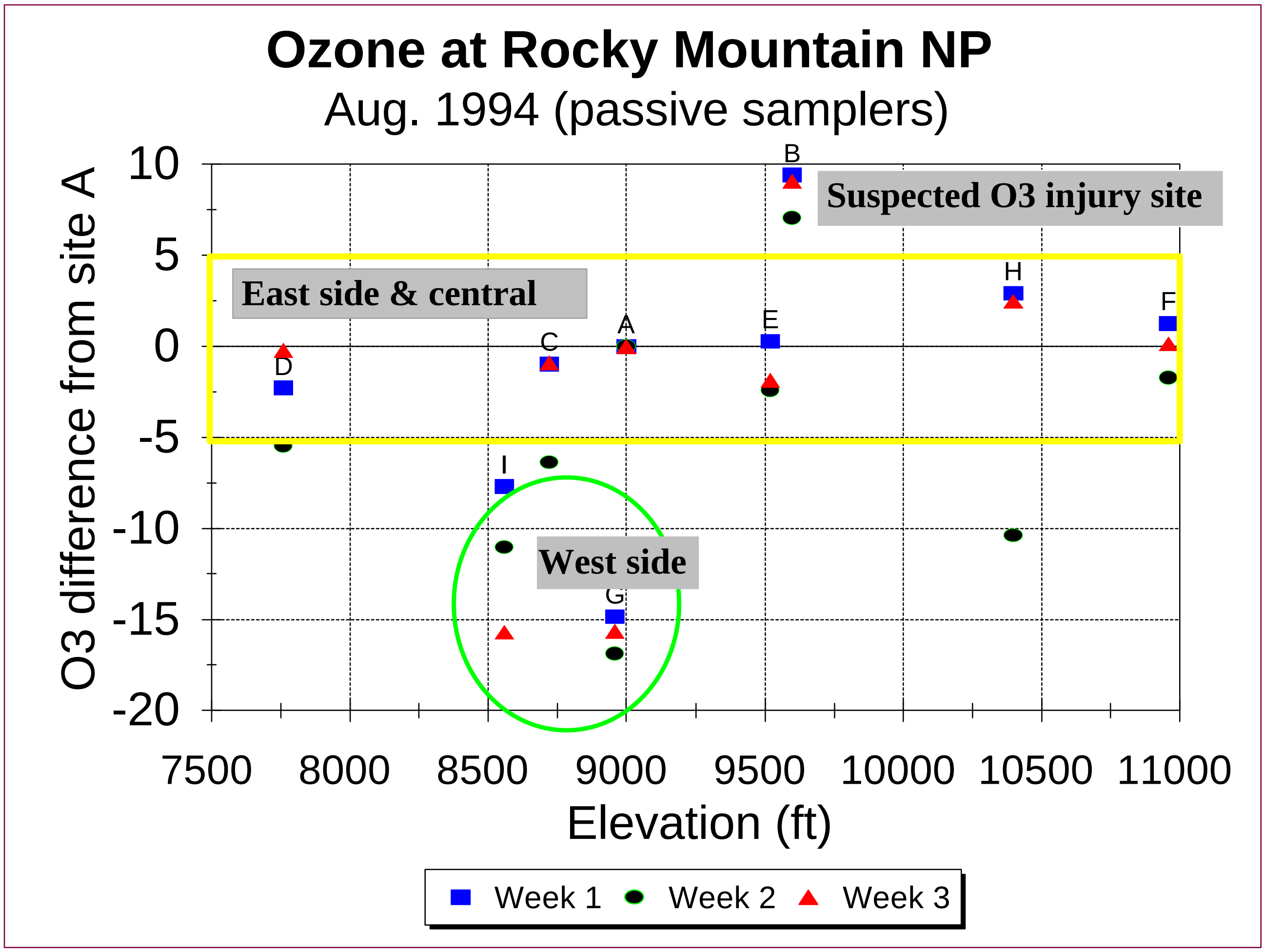


Figure 30 Summary graph showing how each location differed from the continuous ozone monitoring station and arranged by elevation.

Most of the sampling locations on the east side and the central portions of the park had similar ozone concentrations. These parts of the park are affected by pollution from the urban and industrial source areas to the southeast along the "Front Range" of Colorado. The western side of the park has significantly cleaner air that is transported from relatively less developed areas to the west. One high-elevation site in the Wild Basin area had higher concentrations than the continuous monitoring site. Excessive tree-nettle yellowing had been noted at this site previously, however, an ARD plant expert was unable to confirm that ozone was the cause. Further study would be required assign a cause to the apparent tree injury.

This study, although short, clearly illustrates that the continuous ozone monitoring station in Rocky Mountain National Park is representative of only a limited area. The more mountainous and complex the terrain, the more likely that ozone concentrations will vary. In this case, the monitoring station appears to represent an area within 10-15 miles of the site on the east side of the mountain range. Unlike other places that have been studied with the passive samplers, an ozone concentration gradient with elevation was not observed. The limited time frame of this study makes it difficult to know if a concentration-elevation gradient develops at other times.

Conclusions

The passive sampling program has provided baseline data of ozone pollution levels in parks not previously included in the ARD monitoring network. As can be seen from the spatial distribution studies, ozone concentrations can vary considerably both within a park (Olympic and Rocky Mountain NP are examples) and also between parks that are fairly close (Colorado Plateau parks). Other NPS ozone-monitoring stations in nearby parks were of limited use in determining ozone concentrations for the parks in this program.

No exceptionally high ozone concentrations were found in parks that participated in this program that did not already have at least one continuous ozone monitoring station. Maximum weekly average ozone concentrations above 70 ppb (Great Smoky Mountains and Sequoia -Kings Canyon NP) should be of some concern because sites with these levels are likely to have exceeded the newly proposed national primary standard of 80 ppb over 8-hours. Parks where the average ozone concentration for the season exceeded 60 ppb (Great Smoky Mountains and Sequoia -Kings Canyon NP) are likely to be exceeding what was proposed for a new secondary ozone standard (sum 60 ppb if >= 25,000 ppb-hr over 3 months). It is concluded that the passive samplers are able to identify areas with high ozone pollution and that most of the sampled areas have ozone concentrations below the recently proposed EPA standards.

We are still learning how to use the passive samplers and how to tease the information out of the numbers we obtain with these devices. In future reports we hope to use statistical distributions to predict seasonal 1-hour maximum ozone concentrations for each of the parksparticipating. The challenge is to relate the passive sampler results to the National Ozone Standards and to the kind of ozone dose information that has proven useful in predicting plant injury (Sum60 or W126, for example). Meanwhile, comparisons between ozone monitoring stations are useful; figures 5 and 6, for example, allow nearby sites and other areas of the country to be compared. Detailed results by week for both years are available in the appendix and may be compared to statistical summaries of other parks that appear in the Annual Data Summaries that are published by the Air Resources Division.

Acknowledgements

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Support Documents

Copies of the support documents for passive sampling are available on request from John D. Ray, (303) 969-2820.

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